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ENVIRONMENTAL HEALTH SERIES

Water Supply
and Pollution Control

WASTE-WATER RENOVATION

Part 1. A Design Study of Freezing
and Gas Hydrate Formation

Part 2. Feasibility Tests of Freezing

AWTR-4

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Advanced Waste Treatment Research Publications

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	Part 1. A Design Study of Freezing and Gas Hydrate Formation	
	Part 2. Feasibility Tests of Freezing	

WASTE-WATER RENOVATION

Part 1. A Design Study of Freezing and Gas Hydrate Formation

by

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Part 2. Feasibility Tests of Freezing

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for

The Advanced Waste Treatment Research Program
Basic and Applied Sciences Branch
Robert A. Taft Sanitary Engineering Center

A combination of reports submitted in fulfillment of contracts (Purchase Order No. 2439 and Contract No. SAph 76969) between Dr. Allen J. Barduhn and Applied Science Laboratories, Inc., respectively, and the Public Health Service. Part 1 was submitted to the Public Health Service in July of 1961; Part 2 was submitted in January of 1962.

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Division of Water Supply and Pollution Control

Cincinnati, Ohio

October 1963

The ENVIRONMENTAL HEALTH SERIES of reports was established to report the results of scientific and engineering studies of man's environment: The community, whether urban, suburban, or rural, where he lives, works, and plays; the air, water, and earth he uses and re-uses; and the wastes he produces and must dispose of in a way that preserves these natural resources. This SERIES of reports provides for professional users a central source of information on the intramural research activities of Divisions and Centers within the Public Health Service, and on their cooperative activities with State and local agencies, research institutions, and industrial organizations. The general subject area of each report is indicated by the two letters that appear in the publication number; the indicators are

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Public Health Service Publication No. 999-WP-4

ADVANCED WASTE TREATMENT RESEARCH PROGRAM

The Advanced Waste Treatment Research Program of the Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems, and the other, more startling in concept, is to renovate waste water for direct and deliberate re-use.

Conventional water and waste treatment practices have little or no effect on many simple inorganic salts and permit an ever-increasing number and amount of highly complex, synthetic organic wastes to contaminate drinking water supplies. If we are to protect these water supplies for the future, it is mandatory that new technologies for water and waste treatment be developed.

Advanced Waste Treatment may be looked upon as a two-step process: (1) Separating concentrated contaminants from the purified water "product," and (2) disposing of the concentrated contaminants in a way that will render them forever innocuous. This "permanent disposal" of separated wastes is essential so that useable surface or ground waters will not be contaminated and so that the same contaminants need not be removed again and again from water supplies.

In one step, then, advanced waste treatment, i.e., water renovation, could alleviate both water pollution and water supply problems — problems of increasing concern both in this country and in the rest of the world. The importance of advanced waste treatment was recognized by Congress in its 1961 amendments to the Federal Water Pollution Control Act (Public Law 87-88). This act directs the Secretary of Health, Education, and Welfare "...to develop and demonstrate practicable means of treating municipal sewage and other water-borne waste to remove the maximum possible amounts of physical, chemical, and biological pollutants in order to restore and maintain the maximum amount of the Nation's water at a quality suitable for re-use."

It is too early to predict accurately the cost of advanced waste treatment technology, but the need is inevitable. Because of population increase and industrial expansion, we are approaching the time when our rivers and streams will no longer be able to assimilate our wastes and when there will be no more developable supplies of fresh water. Whatever the cost of this technology, one thing is certain — it must be the very lowest science and

engineering can achieve. Anything more will impose an inexcusable, perhaps intolerable burden on our country's economic growth and on its ability to compete in tomorrow's world.

The author of Part 1 of this report, Dr. Allen J. Barduhn, of Syracuse University, has been consultant to various industries and agencies in the desalination of sea water by freezing or gas hydrate formation since 1958. He has published many important papers in the field.

Under the direction of Dr. Arthur Rose with the assistance of Mr. Robert F. Sweeny, coauthors of Part 2 of this report, Applied Science Laboratories, Inc., has been doing research on sea water demineralization since 1954. A 40-gallon-per-day pilot plant has been designed and constructed, and this equipment was used during this contract.

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ABSTRACT

The freezing and gas hydrate processes for demineralizing sea water are adapted in a preliminary design to renovate municipal waste waters. Assuming a feed material containing 1,000 parts total dissolved solids per million, the author (Part 1) predicts costs for recovering 92 percent of the feed as potable water (250 ppm TDS). The waste stream can be further concentrated under eutectic conditions to produce more water and a waste stream of damp solids. Cost of disposal of the concentrated waste stream is not included in either case.

In 14 actual freezing tests completed (Part 2), chemical oxygen demand (COD) was reduced 65 to 85 percent; chlorides, 85 to 90 percent; and conductivity, 90 percent or more. Reduction of alkyl benzene sulfonate (ABS) was erratic. The isobutane used as a refrigerant interfered in the COD tests. With data from the better test runs, preliminary cost estimates indicate that 95 percent of the feed water containing 10 percent of the contaminants can be recovered at a cost somewhat lower than that predicted for desalinating sea water by freezing.

WASTE-WATER RENOVATION

Part 1. A Design Study of Freezing and Gas Hydrate Formation

SUMMARY

The freezing and the gas hydrate processes for demineralizing sea water have been adapted to reclaim fresh water and remove dissolved solids from municipal waste water.

Either the freezing or hydrate process can be used to reclaim most of the water in waste water by concentrating the dissolved solids to about 1 percent and disposing of this residue. The fresh water can have any dissolved-solids content down to about 100 ppm, but 250 to 500 ppm is more economical. The estimated cost of the fresh water produced is about \$0.40 per 1,000 gallons (including the cost of complete conventional treatment), a price considerably higher than now paid by most cities, but not far from what will be paid by southern Californians within the foreseeable future for importing and purifying water plus treating the resultant waste water. This process is suitable, however, only where large volumes of concentrate (1 percent dissolved solids) may be readily disposed of.

When it is necessary to concentrate the dissolved solids to a much greater extent, a second process, devised to remove the dissolved material in solid form, can be used. This process is called the eutectic process and involves removing water and solids simultaneously, at temperatures around -10°F , if eutectic freezing is contemplated, and at temperatures considerably above -10°F if eutectic hydrating is employed. The freezing process, by removing most of the water from waste water at higher temperatures and then treating the remaining 8 percent at the lowest temperature, results in a cost of about \$0.50 per 1,000 gallons of water produced.

It is predicted that the eutectic processes will remove most of the ABS and other organic materials of high molecular weight, as well as the inorganic salts, because the large concentration of salts will force the organic materials out of solution at the low temperatures used.

The final, rejected, wet, solid residue will have a volume of one-thousandth that of the feed, but the problem of treating or disposing of this residue has not been considered.

THE PROBLEM

The search for new sources of water and the necessity for controlling the pollution of rivers by waste water lead naturally to the idea of solving both problems simultaneously by separating the contaminants from the pure water and then re-using the water. The contaminants should be recovered in a rather concentrated form so they can be disposed of by some means other than discharging them into waterways.

Several processes come to mind that could accomplish this objective, the simplest being to evaporate the water and leave dry solids. The drawback to this idea (and most of the others) is simply that it is now too expensive. The Public Health Service's Advanced Waste Treatment Research Program is concerned with the problem of finding economical methods for treating waste water to the extent needed for its re-use. What is economical today and what will be economical 10 years hence are two different things, however. The price we are willing to pay for water will inevitably increase, and the cost of producing water by new processes will inevitably decrease, as time passes, and the amounts will be equal at some time in the future. This point will be different for each community, and it will depend on the relative demand for and scarcity of water. It has already been reached in several places in the world, such as the island of Aruba, where water is scarce and the need great. Water is produced there by the multiple effect evaporation of sea water at a cost of about \$1.75 per 1,000 gallons. The town of Coalinga, California, now treats brackish water by electrodialysis to make potable water at a cost reported to be \$1.46 per 1,000 gallons. These costs are roughly one order of magnitude higher than that for water from conventional sources. It is fairly certain that many communities in the United States will be treating their own waste water to remove contaminants and to make potable water in the next decade or two.

At costs somewhat beyond those for conventional waste-water treatment, it is possible to reclaim about 90 percent of the water from waste water by some processes now considered for desalting sea water, such as multiple-effect evaporation, vapor recompression, freezing, or gas hydration. In some cases, these processes may be acceptable ways to reclaim water, but they depend on the existence of a place to reject the concentrated contaminants. Coastal communities may, in some cases, reclaim 90 percent of their waste water as fresh water and reject the remainder into the ocean.

This solution of the water problem is, in itself, of no use to inland cities, especially those that share a river with other communities, since it does nothing to improve the soluble-solids content of the total effluent of the community. Each community adds its share of refractory contaminants (those that are not removed by any conventional treatment), and the water problems of the towns downstream become progressively more acute. What must be done is to remove suspended and soluble solids from the effluent at the same rate they are introduced by usage and to reject these solids in some manner that does not reintroduce them into the surface- or ground-water supplies. This report is not concerned with methods of getting rid of solids once they are separated, but with simplifying the disposal problem by separating the soluble solids in as concentrated a form as possible.

A large city that treats 100 million gallons per day (100 mgd) of waste water for re-use by concentrating the dissolved solids by a factor of 10 (reclaiming about 90 percent of the water) has the problem of disposing of 10 million gallons per day of waste with a solids concentration of about 0.5 to 1.5 percent. This waste cannot be simply buried. Concentration by another factor of 10 will yield 1 million gallons per day containing about 10 percent solids, but this still poses a difficult problem. It can be simplified, however, by removing even more water. A final residue of bone-dry solids would have a volume of about 50,000 gallons per day. Organics in this residue can be burned out, and salts may be recovered for industrial use.

NATURE OF WASTE WATER

The aqueous effluent from a community is, almost always, at least 99.8 percent spectroscopically pure water, but the few hundredths or tenths of a percent of contaminants make it unsanitary, distasteful, and usually unfit, even for industrial or agricultural use. The contaminants may be broadly classified as suspended matter and soluble matter. Suspended materials may be removed by relatively simple and inexpensive means, called primary treatment. Some of the dissolved and colloidal organic matter may be removed by various processes, called secondary and intermediate treatments. These processes are used to make the waste water suitable for discharging directly into streams, but they do not make it fit for general re-use, though, in some cases, this treated water has been re-used for agricultural or industrial purposes. Generally, it may not be re-used repeatedly for any purpose. Any municipality contemplating continuous re-use of its effluents must provide for the continuous removal of soluble solids in a fairly concentrated form. It has been pointed out that "a single municipal use of water produces an average increment, even after complete treatment, of about 300 ppm of total dissolved solids (TDS)."¹

The salts in waste water are made up mainly of the cations Na^+ , K^+ , Ca^{++} , and Mg^{++} , and the anions Cl^- , $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, and HCO_3^- . Frequently, the salts $\text{Ca}(\text{HCO}_3)_2$ or NaCl predominate. Large concentrations of the former yield hard water, and the presence of the latter in large concentrations is detrimental when the water is to be used for agricultural purposes. Most inorganic salts are refractory contaminants. Stone and Merrell¹⁸ give analyses for inorganic salts of the untreated waste water from about 17 communities. The mean total of dissolved solids is about 600 ppm and the range is mainly 400 to 1,600 ppm. Of this total, about 80 percent appear to be inorganic salts. The increment of total dissolved solids added by a single use, quoted above, shows that about 80 to 90 percent of the solids introduced are inorganic. Analyses by Bunch et al.⁶ show that, in secondary effluents, better than 90 percent of the dissolved solids are inorganic. Raw waste water would show a somewhat lower fraction of inorganics among its dissolved solids.

The composition of the organic part of the refractory contaminants is not as well known as is that of the inorganic part, though some work has been done on this.⁶ Persistent organic solubles include detergents, pesticides, phenols, and other petrochemicals. Other soluble organics are sugars, proteins, acids, and bases. Detergents have the most notoriety, and the extent to which they are removed by secondary treatment is disputable. An activated sludge and sand filter treatment apparently removed 89 percent of the detergents (ABS) at the Los Angeles Hyperion Plant,¹⁸ but others indicate only a 25 to 35 percent reduction¹⁴ with a trickling filter, or at least a 50 percent reduction¹³ with activated-sludge treatment. Primary treatment removes only 2 to 4 percent of the ABS.¹³

In view of the wide ranges in amount and composition of the total dissolved solids (TDS), it would seem impossible to design a plant to remove them that could indicate what can be accomplished. It will be shown later that the amount of TDS in the waste water is not very important, since its concentration in the influent to and effluent from a city recycling much of its waste water for re-use is partly within the control of the designer, and he may set this at will within certain limits. The problem of the composition of the TDS is much more difficult, and a considerable amount of research will be necessary in the future, not only to identify the soluble organics and inorganics, but also to determine how each behaves in various types of tertiary treatment processes. This problem will be discussed further in subsequent chapters.

THE FREEZING AND HYDRATING PROCESSES

The freezing and hydrating processes are designed to remove pure water from its aqueous solutions. Both do this by precipitating water as a solid, washing the solid free of mother liquor, and then melting the solid to release pure water. Both processes are newer than the evaporation methods or even the electrodialysis method for purifying water, but appear to be strong contenders for desalting sea water on a large scale. The cost of obtaining fresh water from the sea has been estimated by Blaw-Knox⁴ for freezing and by Koppers¹² for the propane hydrate process to be about \$0.50 per 1,000 gallons of fresh water produced.

Figure 1 is a simplified flow diagram that may serve for either process. The freezing process will be outlined first. The feed is de-aerated and then pre-cooled by exchange with cold product. It is then introduced into a vessel (freezer or reactor) where it directly contacts an immiscible, boiling refrigerant such as butane. Ice forms as small particles, and a slurry of brine and ice is pumped to a washing system. Recirculation of brine to the freezer controls the ice concentration (normally 5 to 10 percent) in the slurry. The temperature in the freezer is the freezing point of the brine less about 2°F. In operation on sea water with 40 percent of the water to be removed, the temperature is about 26°F. In the washer about 5 percent of the net fresh-water product is used to free the ice of salt.

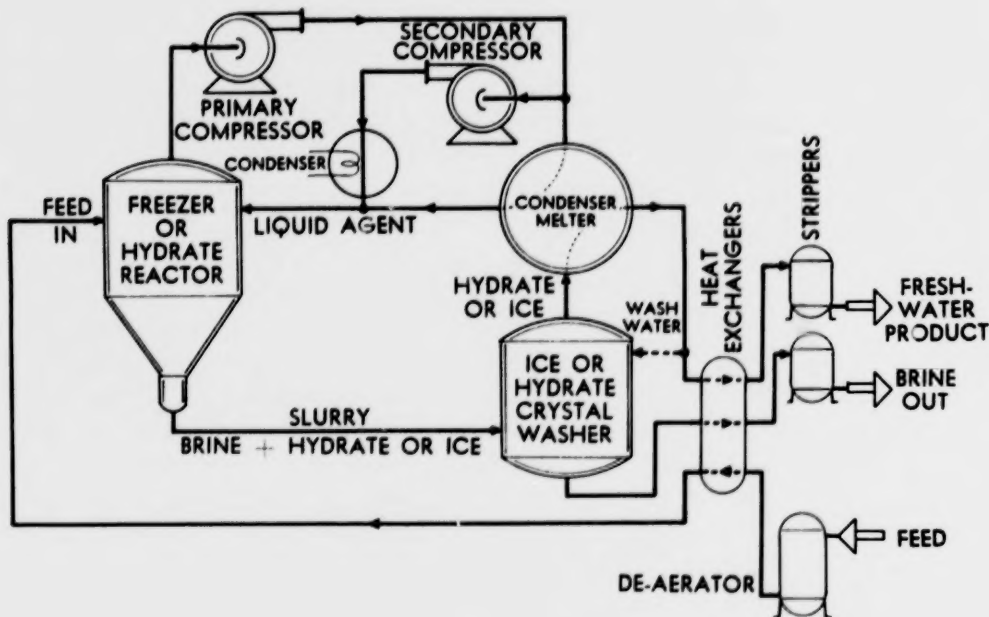


Figure 1. Schematic flow diagram. Freezing and hydrating processes.

The vaporized refrigerant is compressed to a pressure adequate to condense it on ice at a reasonable rate. This is the saturation pressure of the refrigerant at about 34° F. The ice is melted and the refrigerant is condensed in direct contact with each other; the water is removed as product and the condensed refrigerant is returned to the freezer. Not all the refrigerant can be condensed on the ice, owing to introduction of heat to the process by incomplete heat exchange and by the heat contribution of the pumps and compressors. This heat must be rejected to the atmosphere by the secondary compressor, which uses about 30 to 40 percent of the total energy for the process.

In the hydrate process, water solidifies as a gas hydrate at temperatures well above the freezing point of water. From the viewpoint of thermodynamics, the hydrate process is a high-temperature freezing process. Certain substances, such as propane, methyl bromide, ethyl fluoride, and many other halogenated methanes and ethanes that are insoluble in water, form a solid crystalline compound with water, containing 85- to 95-mole percent H_2O , under certain conditions of temperature and pressure. This compound is called a gas hydrate, and it can be used in place of ice to separate water from its aqueous solutions. The hydrating agent is so chosen that it will both form the solid compound with water and be an economical refrigerant.

Figure 1 is the flow diagram for this process also. The difference between the two processes is that the higher temperatures used in the hydrate system reduce the energy requirements for the secondary compressor and reduce the extent of the heat exchange surface required. Each of these factors contributes strongly to the cost of water produced, but it is possible to eliminate them from consideration by means of hydrates that form at ambient temperatures. Other considerations such as the solubility of the agent in water (usually less than 1 percent), the formation pressure of the hydrate, and the cost of the agent also affect the choice of hydrating agent.

The main advantages of both these processes are:

1. There is no scaling problem, which attends all vaporization processes.
2. There is no need for membranes or other devices difficult to make and maintain. All the equipment is conventional.
3. The direct contact heat exchange in the reactor and in the condenser-melter allows very small temperature differences for heat transfer, and this, coupled with the low heat of fusion of ice and hydrate (compared to the

heat of vaporization of water), yields low energy transfer requirements.

Both processes are still in development. The largest plant now operating is designed for only 35,000 gallons per day (Blaw-Knox) via freezing. No complete pilot plants have yet been built using the hydrating process, though Koppers is designing one. The predicted costs of water for these processes are unproved estimates.

From the standpoint of thermodynamics, the hydrate process is cheaper, but other factors, such as the kinetics of hydrate formation and the problem of crystal size, may counteract this.

More detailed information may be obtained on the freezing process,^{5,9} the hydrating process,^{3,10} and on a comparison of them.¹⁹

The Office of Saline Water has designated that the freezing process be used in its fifth demonstration plant, to be built at Wrightsville Beach, N. C. Several variations on this process have been made by various groups, such as Carrier Corporation, Cornell University (H. F. Wiegandt), Blaw-Knox, Struthers-Wells, the Japanese Government (Umano), and Zarchin of Israel (with Fairbanks-Whitney).

The hydrating process is not so far advanced as the freezing process. Barduhn et al.^{2,3} have worked on the thermodynamics of the hydrates, and the Koppers Co., which has patented the propane hydrate process, has done some pilot plant work.¹⁰

These processes are now considered useful only for removing water from its aqueous solutions. They will be adapted later to remove soluble materials from waste water (p. 18).

ADVANCED TREATMENT OF WASTE WATER BY FREEZING OR HYDRATING

Recovery of Pure Water Only

When recovery of pure water from waste water is the only objective, and the disposal of fairly large volumes of concentrated residue is no problem, the freezing and hydrating processes are easily adapted. In these circumstances, it will probably cost less to make a gallon of pure water from waste water than from sea water.

PRETREATMENT

Practically all the suspended matter must be removed before freezing because the solid particles tend to clog an ice or hydrate bed during washing. Furthermore, solid particles provide an excessive number of nucleation sites in the reactor or freezer, which yield a large number of small crystals that are more difficult to wash than are a small number of large crystals. Moreover, suspended matter will not be removed by these processes; it must be filtered out before the water is re-used.

Whether a secondary treatment is necessary depends mainly on the requirements for control of pollution by the effluent. Freezing or hydrating of waste water to produce water only probably will not even kill bacteria. This depends partly, however, on the nature of the refrigerant used. Normal butane, the most common refrigerant for freezing, probably has no germicidal properties. Propane, methyl bromide, and Freon-31 (CH_2ClF) are likely hydrating agents, and the halogenated compounds may have some action on bacteria.

Both processes are carried out in the absence of air. The feed streams must be de-aerated (degassed) because fixed gases in the melter-condenser impair the condensing process. De-aeration may also affect the bactericidal action of the processes.

OPERATING CONDITIONS

Generally, the two processes being considered for water recovery remove from waste water both potable water and a substantial amount of suspended material, if this material is not removed in a pretreatment. The processes leave intact most of the dissolved materials, both organic and inorganic. The final product will have some TDS remaining in it; the amount depends on the designer's choice. It will probably be difficult to reduce the TDS in the final water below 100 ppm. Values of 250 to 500 ppm, however, are not unreasonable.

The concentration of TDS in the rejected residue is also a matter of choice and depends mainly on the fraction of the waste water to be recovered as pure water and on the economics of the process.

For the sake of discussion, and as illustration of a worst possible case, let it be assumed that 10 million gallons per day of waste water has been treated at least for removal of suspended material, that the TDS amounts to 1,000 ppm, and that the pure water product from the tertiary treatment is to contain

250 ppm TDS; the concentration of TDS in the residue will then be related to the percent recovery of fresh water (Table 1).

Table 1. CONDITIONS FOR RECOVERING FRESH WATER AT 250 ppm TDS FROM 10 mgd OF WASTE WATER CONTAINING 1,000 ppm TDS

TDS in rejected residue, ppm	Approx vol of rejected residue, mgd	% of feed recovered as fresh water	Approx vol ratio of feed/reject	Temperature lift for primary compressor, °F
2,000	4.3	57	2.3	4.2
5,000	1.6	84	6	4.5
7,500	1.0	90	10	4.8
10,000	0.8	92	13	5.0
20,000	0.4	96	26	6.0
50,000	0.15	98	67	9.0

It is possible to determine the probable operating conditions, knowing some of the characteristics of the processes. Most of the energy required goes to the two compressors. Consumption by the secondary compressor depends mainly on the feed rate of waste water to the plant, the approach temperature in the heat exchangers, and the difference between the cooling-water temperature and the melting temperature of ice or hydrate. All these factors are fixed for the problem at hand, and thus the energy for the secondary compressor will be little affected by how the feed is split into purified water and rejected residue, as long as the rejected brine concentration does not exceed a few percent.

The energy for the primary compressor depends mainly on the amount of fresh water produced and the temperature lift required. For a fixed feed rate of waste water both these factors will change as the percent of the feed recovered as fresh water varies. Rough calculations show that the economical amount of water to recover is between 90 and 96 percent of the feed. This seems logical, since at least half the cost of the plant is determined by the feed rate, and the objective is to get as much product as possible from this investment. Only with high recoveries (say greater than 96 percent), does the cost of operating the plant overshadow the small increment of product. It is concluded that TDS in the rejected residue would most likely be between 0.75 and 2.0 percent (7,500 to 20,000 ppm). The assumption here is that the disposal of this concentrated residue is no problem. If it were, much larger concentrations would be needed to reduce the volume of the rejected solids.

To arrive at the above figures, it was necessary to assume freezing points for various concentrations of dissolved materials. Since no data could be found on freezing temperatures of waste water some estimating was involved. On the assumption that the organics have rather high molecular weights and comprise only 10 to 20 percent of the TDS, they will not affect the activity of the water nearly as much as will the inorganics. The inorganic species present are the same as those in sea water, though the proportions are different, especially for bicarbonate. The depression of the freezing point or temperature for hydrate formation owing to sea salts is close to 1°F per weight percent salts up to a few percent total salts. We would thus expect TDS to show a depression somewhat less than this, e.g., about 0.8 to 0.9°F per weight percent TDS. A safe estimate would be 1.0°F per weight percent TDS, and this has been used above.

One other question arises. If 90 percent of the water from waste water is precipitated as ice, is anything else precipitated? The residue is concentrated by a factor of about 10 and the TDS is about 7,500 ppm. It is not likely that the solubility of sugars, acids, bases, ABS, etc. will be exceeded. With some of the inorganic salts, the opposite may be true. The salts of sodium and potassium will surely stay in solution, but the calcium salts are not nearly as soluble. In pure water at 32°F , calcium carbonate, bicarbonate, and sulfate have solubilities of 13, 1,615, and 1,759 ppm respectively. In those waste waters in which CaSO_4 comprises over about 20 percent of the TDS, or in alkaline solutions, CaSO_4 or CaCO_3 may be expected to precipitate with the ice. The solid salts may be made to leave with the reject stream by settling the slurry from the freezer before pumping it to the washer. Hopefully, the ice will float and the calcium salts will sink. In the freezing process, if this gravity separation is not effective, and in the hydrating process, in which the hydrate crystals usually sink, the solids salts would have to be separated by elutriation or some other solid-solid separation technique.

ENERGY AND MATERIAL BALANCES

Energy and material balances are determined for a plant treating 10 million gallons per day of waste water at a TDS of 1,000 ppm, with the treated water containing 250 ppm, and the rejected stream containing 1 percent TDS. Figure 2 shows the flow rates and energy requirements based on the assumptions shown in Table 2.

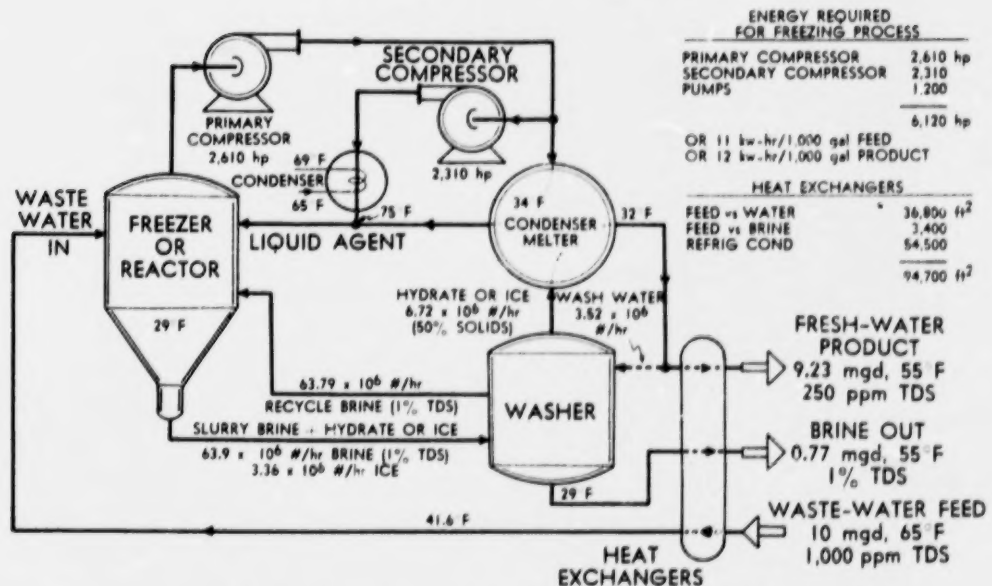


Figure 2. Schematic flow diagram. Advanced waste treatment for water recovery only; freezing or hydrating process. (Heat and mass balances shown for freezing process only).

Table 2. ASSUMED CONDITIONS FOR ADVANCED TREATMENT OF 10 mgd WASTE WATER BY FREEZING FOR WATER RECOVERY ONLY

Compositions

Feed.....	1,000 ppm (0.1%)	TDS
Product water.....	250 ppm (0.025%)	TDS
Rejected residue.....	10,000 ppm (1.0%)	TDS
Slurry leaving reactor.....	5% ice by weight	

Temperatures

Feed.....	65° F
Products.....	55° F
Cooling water.....	65° F with 4° F rise
Heat rejected to cooling water at.....	75° F

Temperature differences

Freezing-point depression.....	1° F per wt % TDS
Driving force for ice growth.....	2° F
Driving force for condensing and melting.....	2° F

Refrigerant: isobutane

Wash-water consumption: 5% of net product water

Compressors: 80% efficient over-all

Heat transfer coefficients

Condensing refrigerant vs cooling

water.....	125 Btu per hr per ft ² per °F
Product vs feed exchange.....	200 Btu per hr per ft ² per °F

The temperatures, flow rates, and energy additions are based on the assumption that the freezing process uses isobutane as the refrigerant. The flow diagram and the flow rates would be practically the same for the hydrate process, but the reactor (freezer) temperature would be higher and the secondary compressor energy requirement and heat exchanger areas would be smaller than shown. The magnitude of these three quantities depends strongly on the hydrating agent used, as in Table 3.

Table 3. HYDRATING AGENTS

Hydrating agent used	Reactor temperature, °F	Approx total area of heat exchangers, ft ²	Approx power required for secondary compressor, hp
None (ice)	29	95,700	2,310
F-21 (CHCl ₂ F)	44	77,000	1,500
Methyl bromide	54	65,000	920
F-31 (CH ₂ ClF)	60	58,000	600

The power requirement for primary compression and the size and design of most of the rest of the plant are nearly independent of the hydrating agent used and are probably substantially the same as for the freezing process.

It would appear then that hydrating is cheaper than freezing, but, because many other factors such as cost of the agent, operating pressure, and agent solubility affect costs, it is not possible, at this stage of knowledge, to choose between freezing and hydrating, or even to choose the best hydrating agent. The final choice will be based on the economy of the various processes, and probably a few years will elapse before enough data are available for the choice. We know most about the freezing process, however, and it is possible to estimate its cost.

COST ESTIMATES

The Estimating Method

The Office of Saline Water has issued a bulletin describing a standard procedure for estimating costs of saline-water conversion.¹⁵ The procedure is based ultimately on getting a cost estimate of the principal items of equipment, and, by using factors that account for all the other costs involved, obtaining the total plant cost. The rate of energy consumption is then multiplied by various factors that account for operating costs, and this product is added to an amortized plant cost to arrive at the cost of the water produced.

By analysis and adjustment of this method to conform to some actual estimates of freezing plants ^{4,12} the following simplified formulas have been derived:

$$\$ \left[\begin{array}{l} \text{Total daily cost to own and} \\ \text{operate a plant} \end{array} \right] = 8.1 \times 10^{-3}k + 0.9 \times 10^{-3}P \quad (1)$$

$$\$ \text{ Total plant cost} = 2.55 P \quad (2)$$

where k = kw-hr energy consumed per day
and

P = uninstalled cost of vessels, heat exchangers, pumps, compressors, and drivers in dollars.

The formulas account for installation, erection, and assembly of all equipment, plus piping, instruments, water supply, storage, service facilities, buildings, engineering, site, operating capital, maintenance, labor, payroll extras, overhead, administration, amortization, taxes, insurance, and contingencies. The formulas have been simplified for some small items. They apply reasonably well to both hydrate and freezing processes, but are applicable only when no forms of energy are consumed other than electrical power.

It is also useful to break down the costs of the uninstalled equipment, as found in detailed estimates by Blaw-Knox⁴ and Koppers.¹² Rough costs, for a 10-million-gallon-per-day plant are shown in Table 4.

Table 4. DETAILED COSTS OF EQUIPMENT

Items	Koppers (propane hydrate)			Blaw-Knox (butane freezing)		
	Size	Uninstalled cost	%	Size	Uninstalled cost	%
Vessels	--	\$1.12 million	37	--	\$2.56 million	59
Heat exchangers	465,000 ft ²	1.04	35	330,000 ft ²	0.64	15
Compressors	12,500 hp	0.64	21	11,000 hp	0.76	17
Pumps + drivers	2,400 hp	0.20	7	3,000 hp	0.37	9
Total (P)		\$3.0 million	100%		\$4.33 million	100%
kw-hr/day (k)		227,000			291,000	
Water cost, calculated (1):		\$0.454/1,000 gal			\$0.626/1,000 gal	
est by company:		\$0.441/1,000 gal			\$0.555/1,000 gal	
Plant cost, calculated (2):		\$7,650,000			\$11,000,000	
est by company:		7,646,000			10,524,000	

The method proposed is seen to agree reasonably well with more detailed estimates, and will be satisfactory for the purposes at hand. Its limitations, stated above, should be kept in mind.

Cost of Water from Waste Water

With equations (1) and (2) above, the cost may now be estimated for producing water from 10 million gallons per day of waste water containing 1,000 ppm TDS, as in Figure 2.

Table 5 gives the rough details of cost of treating waste water to reclaim water only. The heat exchange area for treating 10 million gallons per day of waste water is only 20 percent of that used by Koppers, for two main reasons. First, Koppers fed 25 million gallons per day of sea water or 2.5 times the rate assumed for waste water fed; and second, they used a 4° F mean temperature difference in their feed-product exchangers while a 10°F mtd was used for the waste-water plant. The increased temperature difference decreases the area of these exchangers by another factor of 5. Several other less important differences exist also.

Table 5. COST OF PRODUCING FRESH WATER
FROM WASTE WATER

Equipment items (uninstalled costs)	
Vessels (15% greater than Koppers)	\$1.30 million
Heat exchangers - 96,000 ft ² (Assume 5,000 ft ² per shell and thus \$4.25/ft ²)	0.41
Compressors, centrifugal at \$80/hp (4,920 hp) .	0.40
Pumps (Use mean of Koppers and Blaw-Knox) .	0.29
P	\$2.40 million

Plant cost (2) = \$6,100,000 or \$0.61 per gpd feed

Treated-water cost

Energy requirements: 11 kw-hr per 1,000 gal feed (Fig. 2)

Add 10% for miscellaneous uses:

$$k = (10,000) (1.1) (11) = 121,100 \text{ kw-hr/day}$$

Water cost (1): \$0.34/1,000 gal fresh water

or \$0.31/1,000 gal feed

The cost of \$0.34 per 1,000 gallons is for the freezing treatment only, but includes de-aeration of the feed. Any cost of primary (necessary) or secondary (possible) treatment would add to this about \$0.05 to \$0.10 per 1,000 gallons, resulting in a total cost of about \$0.40 per 1,000 gallons of fresh water reclaimed. This water is, of course, much more expensive than usual, but the cost is comparable with what southern Californians will probably have to pay for combined importation, water treatment, and waste treatment within a few years. It is less than the estimated cost of getting fresh water from the sea, mainly because the water is

removed from a 1 percent salt solution instead of a 6 to 7 percent solution, as is necessary in treatment of sea water. The difference shows up directly in the energy requirements of 12 kw-hr vs 29 kw-hr per 1,000 gallons of fresh water produced (Figure 2).

Recovery of Soluble Solids

Treating waste waters to remove the soluble solids in the most concentrated form possible so their ultimate disposal will be simplified is a very important problem. The fresh water produced will inevitably have a lower TDS than the waste water whenever solids are recovered.

GENERAL FLOW ARRANGEMENTS FOR ANY ADVANCED WASTE TREATMENT

Certain problems in TDS removal are general and will occur regardless of the method used. These have to do with specifying TDS concentrations to and from the city and the treatment plants.

The question of whether conventional treatment is necessary before an advanced process for TDS removal is used depends on the nature of the advanced process. If it were an evaporation process, for example, conventional treatment might not be needed to make the product water bacteriologically or chemically safe, but it might be needed to minimize the fouling of heat transfer surfaces. With the freezing or hydrate processes, the need for complete conventional pretreatment is not known. Secondary treatment, for example, would remove some organic solubles, but whether this simplifies freezing cannot be stated now. A primary treatment plus TDS removal by freezing might perform all the functions of primary plus secondary plus freezing treatment. Some laboratory experiments can determine this.

In the cases to be considered, some of the effluent from the city may be discharged directly to natural watercourses. Since this water, at least, and possibly all feed water to the crystallization process, will require secondary treatment, this treatment will be assumed to be required in all cases.

Two general flow diagrams have been devised for systems that include advanced treatment. The first is applicable when water supply is the only problem, i.e., effluent from conventional secondary treatment can be safely discharged to receiving waters. In this case, advanced treatment is needed only for recycled water. The second diagram is applicable when both water supply and water pollution are problems, i.e., effluent from a conventional secondary treatment plant does not meet quality

standards for discharge to receiving waters. In this case, advanced treatment is needed also for part of the water discharged permanently from the city. Such restrictions on the TDS in discharged effluent do not now exist in any place known to the author; it is assumed, however, that in the future, when multiple re-use of water is common, good pollution control practice will require laws to limit not only the suspended material but also the dissolved material in any effluent discharged into a natural waterway.

The cases are illustrated in Figures 3 and 4, and the conditions that have been fixed arbitrarily are stated in Table 6.

Table 6. CONDITIONS ASSUMED FOR ADVANCED TREATMENT
FLOW DIAGRAMS IN FIGURES 3 AND 4 ^a

Fresh water available from conventional source . .	0 to 100 mgd
City water requirements	100
Waste water from city	100
TDS in fresh-water supply	250 ppm
TDS in city water	250
TDS in raw waste water	1,100
TDS in secondary effluent	1,100
TDS in renovated water	250
Max allowable TDS in effluent to receiving waters:	
Case I	no restriction
Case II	350 ppm

- ^a City's water use is nonconsumptive (water supply volume = waste-water volume).
All raw effluent is given primary and secondary treatment. Solids discharged from primary, secondary, and advanced treatments are highly concentrated.
Quality of water is represented by TDS content; all known biological and toxicological contaminants are selectively and specifically removed from the city water supply.

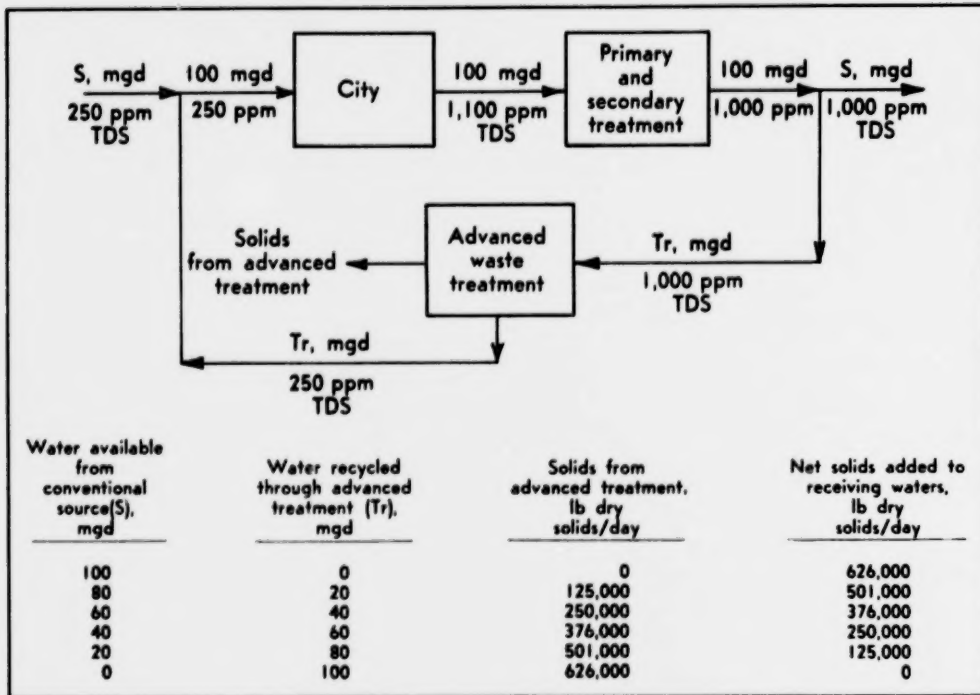


Figure 3. Case I: Flow diagram for recycling renovated water. Water supply is the only problem, i.e., effluent from conventional secondary treatment can be safely discharged to receiving waters. (See Table 6.)

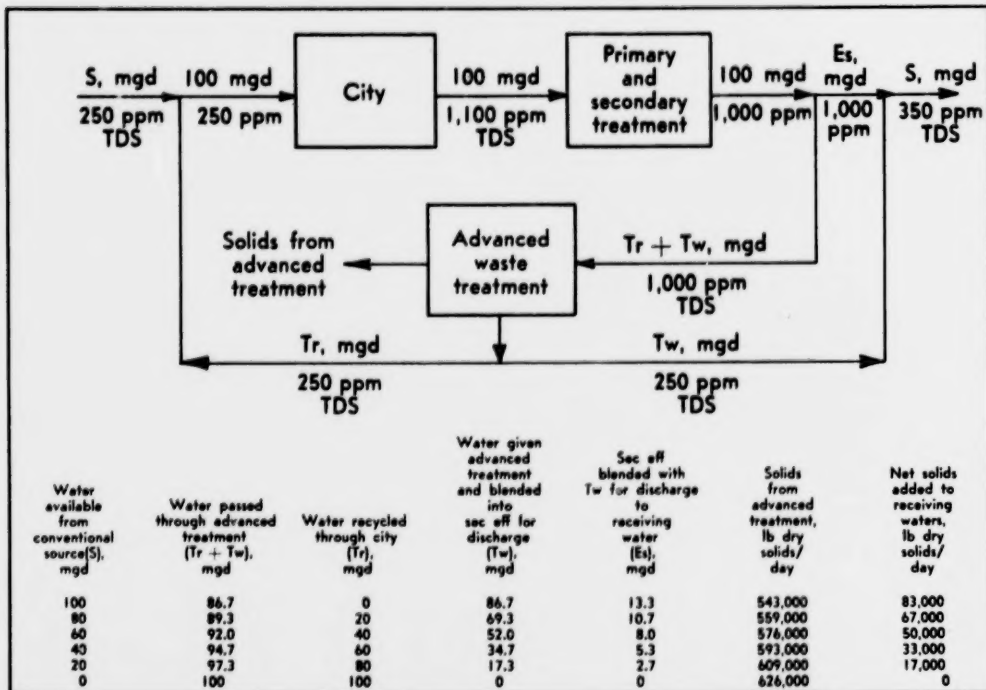


Figure 4. Case II: Flow diagram for recycling renovated water. Both water supply and water pollution are problems, i.e., effluent from a conventional secondary treatment plant does not meet quality standards for discharge to receiving waters. (See Table 6.)

These flow diagrams illustrate the two applications of advanced waste treatment systems: to alleviate water shortages and to minimize water pollution. These figures apply, regardless of the type operation used to remove TDS, as long as the solids are removed in a rather concentrated form—say at least 25 percent concentration.

A PROPOSED METHOD OF SOLIDS REMOVAL BY EUTECTIC FREEZING

It is possible to adapt the freezing process to remove not only water but also soluble solids from aqueous solutions by operation at temperatures low enough to reach the eutectic compositions for the salts to be removed. To illustrate the principle involved, assume that a dilute solution of NaCl is to be treated to remove both water and solid salt by freezing. Figure 5 shows the phase diagram for the system NaCl-H₂O.⁸ When the solution at point (A), for instance, is cooled to some temperature below 32° F (depending on the initial salt content), ice will begin to form. Along the line on Figure 5, this formation is seen to occur at point (B). As more ice is formed by further cooling, the composition of the remaining solution follows the curved path BCD until point (D) (the eutectic point) is reached. Up to this point, only ice has been formed, but further heat removal at the eutectic point (D) results in the temperature remaining fixed at -6° F and both ice and NaCl·2H₂O precipitating in a ratio that maintains the residual liquid at the fixed composition of 23.3 percent NaCl. The two solids formed can be separated by settling since the ice floats and the dihydrate sinks. The ice can be put through the washing process and then melted to yield fresh water, and the dihydrate can be filtered from the brine and rejected. It might be thought that the cost of such a process would be high since large volumes of water and ice will be processed at low temperatures, but it will be shown later that the cost is substantially the same as that for producing fresh water from sea water.

Since waste water is not as simple a mixture as aqueous NaCl solutions, it is necessary to consider the real process of freezing waste water rather than the hypothetical process described above.

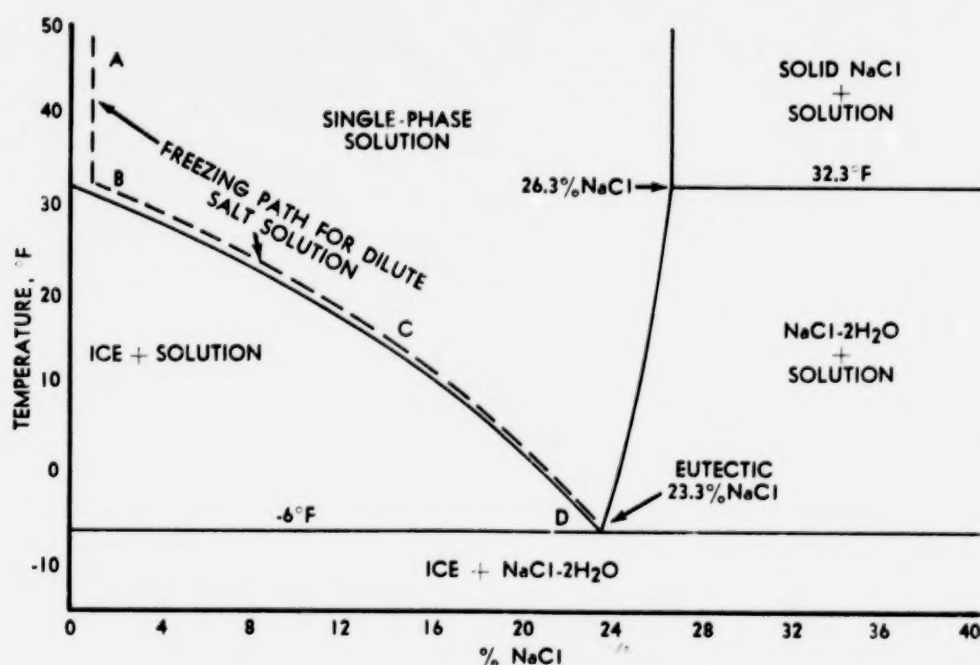


Figure 5. Phase diagram for the system NaCl-H₂O.

THE FREEZING OF WASTE WATER

The Inorganic Salts

The organic solubles will be ignored for the moment while the process of freezing an aqueous solution of several inorganic ions normally found in waste water, e.g., Ca^{++} , Mg^{++} , Na^+ , $\text{SO}_4^{=}$, Cl^- , $\text{PO}_4^{=}$, HCO_3^- , $\text{CO}_3^{=}$, etc. is being considered. When water is removed from such a solution, the solubility of one species is usually exceeded first, and this continues to precipitate with the ice until a point is reached at which the solubility of a second salt is exceeded. Further removal of water (as ice) precipitates salts and ice simultaneously (ternary eutectic) until the solubility of a third salt is reached, and so forth. Eventually, the remaining solution has a fixed composition and temperature, and all the salts precipitate simultaneously. These processes are described well by Kobe,¹¹ who shows phase diagrams for some ternary and quaternary systems.

The salts do not precipitate always as simple anhydrous species. They often appear as double salts or as hydrates. Their relative solubilities in the presence of one another change markedly with temperature, and the nature of such multicomponent systems cannot be predicted in general from the data on individual

species, though some qualitative estimates will be made later. To find what happens to these systems when water is removed requires research on their thermodynamics and phase equilibria. In addition to determining phase diagrams, it is important to determine heats of fusion, crystallization, and solution for purposes of design.

Without such data it is not possible to design completely a plant for eutectic freezing. Because of the peculiar nature of the salts found in waste water, however, it is possible to draw some useful conclusions that will permit enough design work to estimate costs. The peculiarity of the salt system arises from the fact that usually the salts present in waste water, except NaCl, are either not very soluble, or else have steep temperature coefficients of solubility so that, at low temperatures, only NaCl will remain in solution in any appreciable quantities, NaCl is abnormal in that it retains its solubility even at very low temperatures. Figure 5 shows that its solubility at room temperature, 32°F, and -6°F is 26.4, 26.3, and 23.3 percent, respectively. Eutectic temperatures with other salts are shown below in Table 7.

Table 7. NaCl EUTECTIC TEMPERATURES

System	Eutectic temperature, ° F	Composition of eutectic solution	Phases present	Ref
NaCl+H ₂ O	-6.0	23.3% NaCl	Ice+NaCl·2H ₂ O+solution	8
NaCl+KCl+H ₂ O	-9.2	20.2 NaCl 5.8 KCl	Ice+NaCl·2H ₂ O+KCl +solution	11
NaCl+Na ₂ SO ₄ +H ₂ O	-7.0	22.8 NaCl 0.3 Na ₂ SO ₄	Ice+NaCl·2H ₂ O+Na ₂ SO ₄ ·10H ₂ O+solution	17

The low solubility of KCl and Na₂SO₄ in NaCl solutions at low temperatures is noteworthy. The NaCl forces the other salts out of solution, and the ternary eutectics occur at only slightly lower temperatures than does the binary NaCl-H₂O system. These facts permit the prediction that, normally, the lowest temperature to which a eutectic freezing process must go to remove all the inorganic salts necessary will be about -10° F. The process described later uses this temperature in the eutectic freezer. The less soluble salts, such as Ca(HCO₃)₂, CaSO₄, MgSO₄, etc., are likely to have precipitated nearly completely long before this low temperature is reached.

The process of precipitation described above depends on the presence of NaCl in the waste water, and it is interesting to calcu-

late what would occur if this salt were not present in appreciable quantities in the waste water. In this case, many of the solids would precipitate at higher temperatures and the process would be more economical. If a large fraction of the effluent were recycled, however, then the small amounts of NaCl present would not be removed for several cycles, and soon its concentration would build up until the required freezer temperature would again be -10°F . Using a freezer temperature of -10°F seems to be the only safe thing to do.

Another important item to note is that the recovered inorganic solids are not all anhydrous, and bone-dry solids cannot, therefore, be removed with the freezing process. The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ contains 56 percent water, and $\text{NaCl} \cdot 2\text{H}_2\text{O}$ contains 38.3 percent water. It is not known in what form the other salts will precipitate.

In the event that waste water contains an excess of Ca^{++} and Mg^{++} over $\text{CO}_3^{=}$, HCO_3^{-} , and $\text{SO}_4^{=}$, then CaCl_2 or MgCl_2 will remain in solution and may depress the NaCl eutectic temperature far below -10°F . In other words NaCl will not force CaCl_2 and MgCl_2 out of solution. Most natural waters do not seem to have an excess of $\text{Ca}^{++} + \text{Mg}^{++}$ over the necessary $\text{CO}_3^{=}$, HCO_3^{-} , and $\text{SO}_4^{=}$ to combine with them. If they do, the addition of soda ash will rule out processing at temperatures much below -10°F . Two waste-water analyses are combined below to list salts in an assumed order of precipitation. The original data are from Stone and Merrell.¹⁸

<u>Palm Springs</u>		<u>Fontana</u>	
CaCO_3	41 ppm	CaSO_4	129 ppm
$\text{Ca}(\text{HCO}_3)_2$	75	$\text{Mg}(\text{HCO}_3)_2$	34
$\text{Mg}(\text{HCO}_3)_2$	61	NaCl	73
NaHCO_3	65	MgCl_2	<u>18</u>
Na_2SO_4	50		254 ppm
NaCl	<u>85</u>		
	377 ppm		

In the case of Palm Springs, the system would operate probably at -10°F since all the Ca^{++} and Mg^{++} are taken up by carbonate or bicarbonate. In the case of Fontana, 18 ppm of MgCl_2 will probably give trouble by not precipitating. As

recycling continues, the MgCl_2 content will increase gradually. In this case, the addition of soda ash (Na_2CO_3) to the system at the rate of 2,000 pounds per day in a 10-million-gallon-per-day plant will yield MgCO_3 and NaCl , and the MgCO_3 will probably be precipitated by the NaCl . The cost of this soda ash will be \$0.004 per 1,000 gallons treated.

This entire discussion on inorganic-salt precipitation is based on rather meager data on salt solubilities and on waste-water analyses that are rather incomplete. But the general conclusions are undoubtedly sound. Much work needs to be done in this area on both laboratory and pilot plant scales.

The Soluble Organic Materials

Those organic materials in waste water that have high molecular weights, even though they may be fairly soluble, will not appreciably depress the freezing points quoted above. Most are not very soluble in any case and these will probably precipitate along with the inorganics. Materials such as lignins, proteins, pesticides, detergents, etc. fall into this class. In fact it is expected that a high salt concentration (23% NaCl) at low temperature (-10°F) will effectively precipitate these substances nearly quantitatively.

For example, it is known that the solubility of ABS is markedly decreased with decreasing temperature,⁷ and that it is a common organic laboratory exercise to prepare the very soluble sodium benzene sulfonate and precipitate it by adding common salt solutions. The alkyl derivatives should precipitate even more readily. Moreover, the ABS does not form a true solution, but rather a colloidal one,⁷ and the stability of colloids should be reduced in solutions of high ionic strength.

The following experiment was made to test the solubility of ABS in salt. Two teaspoons of "Tide" were added to a glass of water at room temperature with stirring, and 1 teaspoon of salt was dissolved in one-half glass of warm water. Both solutions were settled and decanted but both appeared slightly cloudy. The salt solution was poured into the "Tide" solution at room temperature and a thick white cloud formed that settled in about 5 minutes.

Tide contains 18 percent alkyl benzene sulfonate and fatty alkyl sulfates, and the remainder is mainly inorganic phosphates.⁷ The above experiment was interpreted to mean that some ABS is precipitated, even by a dilute salt solution at room temperature.

Thus, it is predicted that the freezing process for removing inorganic salts will also remove substantial amounts of ABS

and other organics of high molecular weight from solution by salting them out at low temperatures. This idea has such a good chance of working and seems to be so useful that it ought to be pursued soon by some experiments to check it.

If waste water contains any appreciable amounts of highly soluble organic compounds of low molecular weight, such as simple alcohols and acids, these compounds will probably not be removed by freezing. They may accumulate in a recycling water system and eventually build up to some steady-state concentration determined by the stoichiometry of the system. Input of these items is entirely from the city itself. Output occurs in two places. One is with the net effluent from the city and one is with the solids removed by the advanced treatment. This latter output has not been mentioned before but is an important sink for all soluble substances not precipitated by freezing. The solids are rejected in a finely divided state as the filter cake from a continuous filter. These solids retain in their interstices large volumes of liquid that cannot be removed, and this liquid will be rejected along with the solids. The steady-state concentration of the few nonprecipitated solids, both organic and inorganic, will determine the extent to which the -6°F eutectic temperature of NaCl is depressed. In all calculations below, it has been assumed that this depression is 4°F and that the eutectic freezer operates at -10°F .

We can now work out in more detail the design of a plant to remove TDS from waste water by eutectic freezing.

ENERGY AND MATERIAL BALANCES

Preliminary Considerations

Before working out the flow diagram for the eutectic freezing process, it is useful to consider the implications of operating a plant at -10°F , through which enormous volumes of an extremely cheap product (water) are flowing. This operation appears economically infeasible until the possibility of staging is investigated. Freezing in stages means that most of the water is removed at temperatures of about 28 to 30°F and that only a small fraction needs to be treated at -10°F . The process described in Figure 2 will serve well as the first stage. Instead of treatment of all 10 million gallons per day at -10°F , only 0.77 million gallons per day need to be charged to the eutectic freezer. A three-stage process might be even more economical if the volume to be treated is exceptionally large, but this has not been investigated.

In a two-stage process in which 10 million gallons per day at 1,000 ppm TDS is to be treated to yield fresh water at 250 ppm

and solids containing 49 percent bone-dry material, economics will determine the composition of the intermediate stream. Figure 6 shows a comparison of the energy consumptions for three different cases. When the percent TDS in the brine from the first stage is low, the energy required for the first stage is low, but that required for the second stage is high, mainly because the volume of water to go through eutectic freezing is large. As the percent TDS leaving the first stage is increased, the first-stage energy requirement goes up and the eutectic-stage energy requirement goes down, and a minimum for their sum will be some particular value of the percent TDS leaving the first stage.

Figure 6 shows the results of calculations that minimize the energy consumption by varying the percent TDS in the interstage stream. It is evident that, within a rather broad range, the minimum total costs do not vary markedly. Even though Figure 6 shows the best intermediate-stream composition to be 2 percent TDS, 1 percent TDS will be used, because the first stage will then be identical to the plant already described in Figure 2 for water recovery only. Furthermore, the final water cost predicted will undoubtedly be practically the same whether we choose 1 or 2 percent TDS as the intermediate-stream composition.

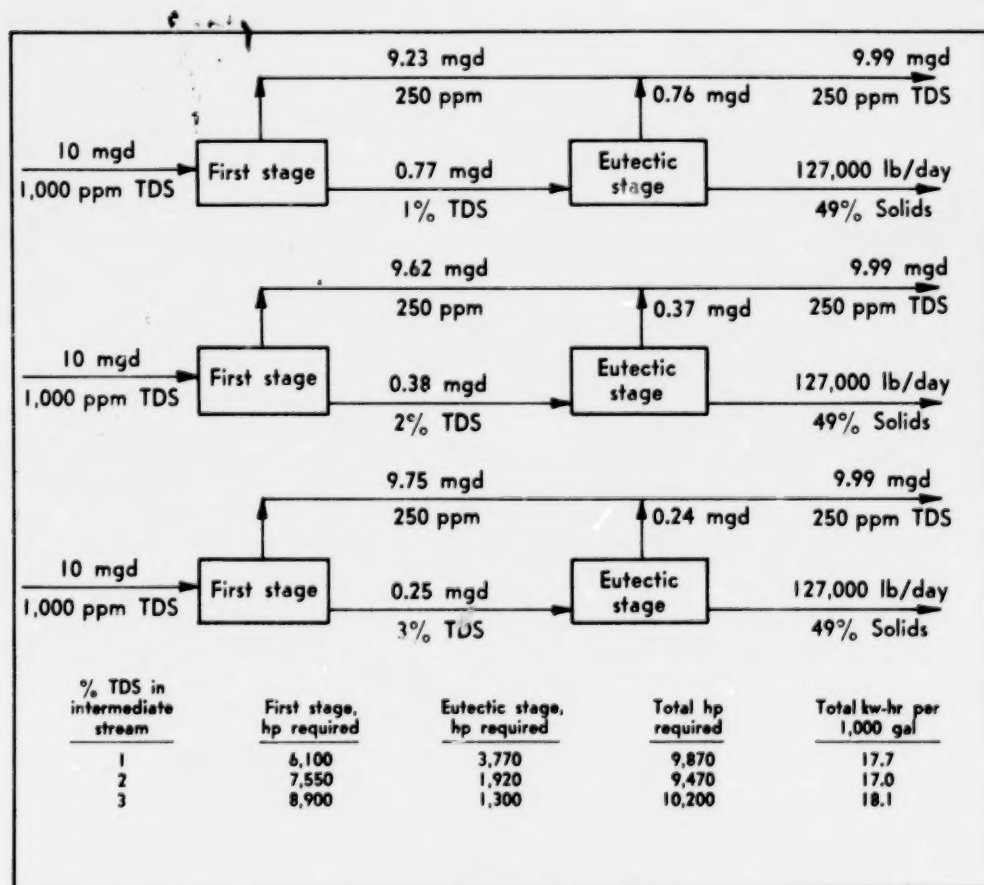


Figure 6. Minimization of energy consumption for two-stage eutectic freezing.

Either the freezing or the hydrate process may be used for stage one, and the comments made previously comparing them apply here as well. If the hydrate phase diagram for waste water contains a eutectic point similar to the one in Figure 5, the final concentration stage could also be either a hydrate or a freezing process. If the hydrate process appears feasible, the operation could probably take place at a temperature considerably above the -10°F required for eutectic freezing. Further research will be necessary to determine the technical and economic feasibility of eutectic hydration. The estimates and flow sheets below are based, for simplicity, on the entire process being a freezing process.

The processes in the eutectic stage will be similar to those in the first stage, with two exceptions. The slurry effluent from the eutectic freezer will contain both ice and precipitated solids, and these two must be separated before further treatment. This can be done in a settling vessel of some kind. A Dorr Thickener is probably best for this purpose. The ice floats in the brine, is recovered as a dilute slurry, and sent to the washer. The solid salts sink and go from the bottom of the thickener to a continuous filter where they are discharged as a moist filter cake while the filtrate is returned to the freezer. If any precipitated organics float in the brine (specific gravity = 1.19 at -6°F), they will leave with the ice, and can be separated by elutriation or some other simple separation process based on particle size and density differences.

Some idea of the compositions of the salts is necessary for making material balances, and, for simplicity, it has been assumed that $\text{NaCl}\cdot 2\text{H}_2\text{O}$ is the only solid present. It has a water of hydration intermediate between anhydrous salts and highly hydrated ones, such as $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$, and is thus representative. Furthermore, there are enthalpy data available on aqueous NaCl solutions down to -6°F that are useful.¹⁶

If it is assumed further that one-third of the filter cake is brine containing 23.3 percent NaCl , and two-thirds is $\text{NaCl}\cdot 2\text{H}_2\text{O}$, the final cake contains 49 percent bone-dry solids. This figure was used throughout the calculations. It may be useful to increase the liquid content of this rejected stream in order to decrease the steady-state concentrations of those materials that do not precipitate under any conditions considered here. The only disadvantage is that the volume of the residue for disposal is increased. With 49 percent solids in the final residue, the TDS will be concentrated from a volume of 10 million gallons per day to about 10,000 gallons per day or by a factor of 1,000. On a weight basis this factor is 650 to 1.

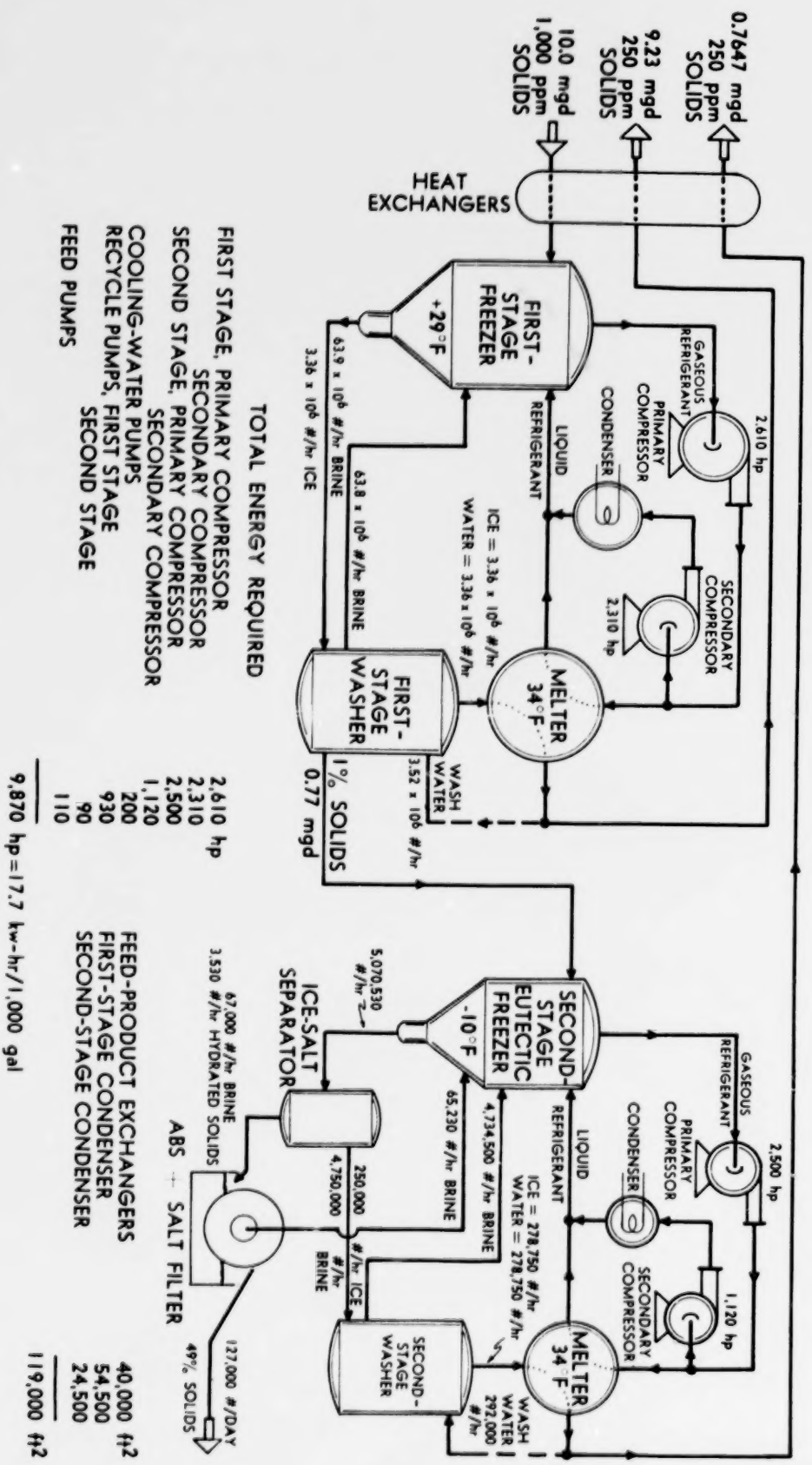


Figure 7. Flow diagram with heat and mass balances. Advanced waste treatment for solids recovery by eutectic freezing.

Flow Diagram and Balances for Eutectic Freezing

Now that the preliminary design specifications have been clarified, a flow diagram with heat and material balances can be made. The design assumptions are listed in Table 8 and the flow diagram is shown in Figure 7.

Table 8. ASSUMED CONDITIONS FOR ADVANCED TREATMENT OF 10 mgd WASTE WATER BY EUTECTIC FREEZING FOR BOTH WATER AND SOLID RECOVERY ^a

Compositions		
Feed	1,000 ppm (0.1%)	TDS
Product water	250 ppm	TDS
Rejected residue	49% bone-dry	TDS
Intermediate brine	1%	TDS
Temperatures		
Feed	65° F	
Product water	55° F	
Residue rejected	-10° F	
Cooling water	65° F with 4° F rise	
Heat rejected to cooling water at . .	75° F	
Primary freezer	29° F	
Eutectic freezer	-10° F	
Refrigerant	n-butane	
Wash-water consumption	5% of net water product	
Compressors		
First stage	80% efficient	
Second stage	75% efficient	
Heat transfer coefficients		
Condensing refrigerant vs cooling		
water	125 Btu per hr per ft ² per °F	
Product vs feed exchangers . .	200 Btu per hr per ft ² per °F	

- ^a Feed is 10 million gallons per day pretreated by both primary and secondary processes.
 Dissolved solids assumed to be pure NaCl for determining heat contents and flow rates.
 Washed ice carries an equal weight of water.

COST ESTIMATES

The method of estimating cost has been described previously. Cost estimates are most easily made by working on each treatment stage separately. The first stage is identical to the plant

previously designed for water recovery only. The conventional vessels for the eutectic stage can be estimated by scaling of the costs with their capacities by use of the 0.6 power rule. The ratio of the throughputs of the first and second stage is 1 to 13, and thus the cost of those vessels that serve identical purposes would be in the ratio of 1 to $13^{0.6}$ or 1 to 4.66, and, if the factor of 0.25 is used, the scaled-down costs would be on the safe side.

Table 9 shows that the estimated cost of reclaiming water from waste water and of removing solids simultaneously is about \$0.50 per 1,000 gallons. This includes the cost of primary and secondary treatment, but does not include any cost for chlorination or the cost of additional pipe to carry water from the effluent site back to the city reservoirs, which may be a considerable expense. This cost also does not include the expense of final disposal of the precipitated solid.

Table 9. COST OF PRODUCING FRESH WATER AND SOLIDS FROM 10 mgd WASTE WATER BY EUTECTIC FREEZING

Eutectic-stage equipment items (uninstalled)	
Vessels	
Those identical to first stage (see Table 5) \$1.30 million + 4	\$0.33 million
Salt-ice separator (Dorr Thickener)	0.05
Filter	0.03
Compressors, 3,620 hp at \$80	0.29
Heat exchangers, 24,500 ft ² at \$5/ft ²	0.13
Pumps	0.07
First-stage equipment cost (uninstalled) (see Table 5)	2.40
Total uninstalled equipment cost (P)	\$3.30 million
Total plant investment (2)	\$8.50 million
Total energy required (k) = 195,000 kw-hr/day incl 10% for miscellaneous uses	
Cost of owning and operating plant (1)	\$4,550/day
Cost of advanced water treatment	\$0.455/1,000 gal
Primary and secondary treatment	\$0.045/1,000 gal
Total cost of water	\$0.50/1,000 gal

The conclusion to be drawn from these cost data is that inland cities facing a water shortage can reclaim and re-use their effluent by giving it a tertiary treatment to remove dissolved solids and produce low-TDS water at a cost about equal to that estimated for producing fresh water from sea water either by freezing or evaporation.

WASTE WATER

The Public Health Service readily admits that the nature of the dissolved solids in waste water is obscure and that a considerable amount of work needs to be done to identify and determine its constituents quantitatively. This is especially true of the organic fraction.

For identifying inorganic ions the paper of Stone and Merrell¹⁸ was used exclusively, but hopefully more complete data will be available for future work. Because of discrepancies in methods now used for solids determination (volatilization, hydrolysis, etc.) present data are inadequate for process development work. To determine whether $\text{HCO}_3^- + \text{SO}_4^{2-}$ are in excess of the $\text{Mg}^{++} + \text{Ca}^{++}$ present, an analysis is needed that shows the solution to be at least electrically neutral. Obviously, more detailed analytical work is needed before it can be known what will happen to waste water on freezing.

The work on waste-water analyses can be augmented by studying directly the effect of eutectic freezing on waste water. One approach would be to freeze out water in stages from a large initial volume of waste water. At the end of each stage there can be determined the TDS in the remaining solution, the amount of ice formed, the amount and the nature of any other substances precipitated, etc. This process can be continued until a temperature of, say, -10°F or lower is reached, and much qualitative and quantitative information on the behavior of waste water in the eutectic freezing process can be ascertained.

INORGANIC SALT SYSTEMS

A considerable amount of work needs to be done on the phase diagrams and on the physical chemistry at low temperatures of multicomponent salt systems. By work on binaries first and then ternaries, etc., eventually a rather complete picture of the system containing the seven or eight ions that commonly occur in waste water can be obtained. These data should be worked out in pure water first before any attempt is made to determine the effects of organics. It may also be useful to get similar data at high temperatures to predict the effects of evaporating water instead of freezing it.

Kobe's description¹¹ of the processing of Searles Lake brine illustrates the importance of knowing the phase diagrams and

physical chemistry of a salt system before recovering salts. The research on these brines after World War I is a good model for waste-water research.

INORGANICS PLUS ORGANICS

Some work needs to be done on solubilities in simple systems containing one inorganic and one organic salt. The behavior of a system such as NaCl + Sodium dodecyl benzene sulfonate or NaCl + common sugar can be used for predicting what will happen in more complex systems. These systems should be studied both at high temperatures (20 to 100°C) and low temperatures (0 to -25°C) to give information useful for both the evaporating and freezing processes.

PROCESSING STUDIES

Once the basic data and the properties of organic and inorganic salts in waste water are known, process studies can be made and pilot plants designed and operated. The problems to be solved include:

1. Determining whether a secondary treatment is useful for the feed to an advanced process;
2. determining methods of separating ice and precipitated organics and inorganics;
3. obtaining design data, such as ice and solid salt formation kinetics in waste water, wash rates in ice beds, filtration rates of precipitated solids, etc.

Economic studies in detail are also needed to determine the best refrigerant and to select the proper process for each stage of the TDS removal. Many more unknowns will come to light as research proceeds.

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Part 2. Feasibility Tests of Freezing

SUMMARY

Fourteen tests were completed on freezing as a method of purifying secondary effluent. The first step in each test consisted of partial freezing to the extent of about 20 percent of the charge, followed by draining off about three-fourths of the mother liquor, which left an ice mush containing about equal quantities of actual ice and mother liquor. The second step in each test was washing the mush of ice and mother liquor with a volume of tap water that ranged from equal to twice the volume of mother liquor in the mush, and then melting the washed mush. In these washing and melting operations the impurities causing COD were reduced by a factor of from about 3 to 7, chlorides were reduced by a factor of about 7 to 10 in the seven tests in which data were taken, and conductivity was reduced by a factor of about 10 or more in over 60 percent of the tests. ABS was reduced by a factor of 5 to 10 in three tests but not in others. The reasons for this erratic ABS behavior are not understood but may be related to concentration of ABS at an interface or surface. The data are summarized in Table 1.

Every freezing process may be thought of in two parts, the first, partial freezing and draining, and the second, washing and melting. The data of this report show that at least the majority of the impurities, and possibly all, are concentrated in the mother liquor and not in the solid ice. The purification by partial freezing and draining depends mostly, therefore, on the percent conversion of charge to ice, and on the percent of the mother liquor that is or can be removed. In a single-step freezing process, only rather limited purification can be achieved by partial freezing and draining because of the practical limits on the proportions that can be frozen and drained. The success of a practical purification process depends mostly on the effectiveness of the washing of the ice mush left after partial freezing and draining. Most of the data of the contract work pertain, therefore, to purification during the washing and melting parts of the tests.

Isobutane expansion directly in the liquid was used to achieve partial freezing in most of the tests because the use of such a refrigerant and procedure was believed to be probably mandatory, for reasons of cost, in an operating plant. It was thought that the final removal of isobutane would be achieved by standard methods and at nominal cost. In this contract, however, the use of isobutane was troublesome because it introduced extraneous and variable amounts of COD, which made COD material balances

Table 1. SUMMARY OF ALL TESTS OF FREEZING AS A METHOD OF ADVANCED WASTE TREATMENT

Test No. (Run No.)	Type of freezing	Type of washing	Type of feed	Remarks	COD in mother liquor, ppm	Concentration ratio, mother liquor to product,			Product purity,			COD material balance, % high			Feed composition,			Washing vs melting b efficiency	
						COD	ABS	Cl ⁻	COD, ppm	ABS, ppm	Cl ⁻ , ppm	Spec cond a	COD, ppm	ABS, ppm	Cl ⁻ , ppm	Spec cond a			
I (5)	Isobutane	Displacement	Natural		210	3.9	1.9	----	5.2	54	1.2	---	133	225	87	2.4	---	670	Melt
II (6)	Isobutane	Spray	Natural		270	4.5	0.6	----	11.7	60	4.0	---	65	286	75	1.7	---	615	Both
III (7)	Isobutane	Spray	Natural	Repeat of II	135	5.0	1.2	----	10.7	27	2.0	---	70	107	57	1.4	---	617	Both
IV (8)	Isobutane	Displacement	Natural	Repeat of I, equipment modified	150	6.5	0.7	----	9.1	23	2.6	---	102	79	80	2.0	---	880	Melt
V (9)	Isobutane	Melt	Natural		87	3.0	0.8	----	4.5	29	2.6	---	168	14	62	2.5	---	690	Not applicable
VI (13)	Isobutane		Tap water		---	----	---	----	----	---	---	---	---	Very high	---	---	---	---	Not applicable
VII (11)	Isobutane	Spray	Natural	Repeat of III	155	4.7	0.8	16.7	20.9	33	3.4	11	58	200	61	3.6	118	865	Both
VIII (14)	Isobutane	Displacement	Foamed		---	16.7	High	10.0	17.6	47	Trace	5	41	1,380	44	0.2	37	580	Melt
IX (15)	CO ₂	Displacement	Natural		125	4.1	4.1	12.6	19.5	30	0.9	4.2	47	48	62	3.4	38	595	Melt
X (16)	CO ₂	Displacement	Foamed	Sample lost, some values estimated	68	3.3	3.6	6.8	12.8	21	0.14	7.1	57	5	58	0.5	48	595	Melt
XI (17a)	Cold wall	Drained only			100	5.1	Very high	7.7	12.6	19	Trace	6	57	2	77	1.4	39	630	Not applicable
XI (18)	CO ₂	Spray	Natural	Contamination possible	90	2.8	8.3	----	----	32	0.2	---	---	18	62	---	---	495	Wash
XIII (19)	CO ₂	Spray	Natural	Special pre- cautions as to contamin- ation	175	7.0	5.8	10.8	18.1	24	1.1	6.0	52	15	133	5.1	47	---	Wash
XIV (20)	CO ₂	Spray	Foamed		110	8.2	1.7	12.0	12.7	14	1.4	4.9	70	0	92	2.2	40	760	Wash

^a Specific conductivity, micromhos per cm, 25°C.
^b This is an approximate indication of which process was responsible for the majority of purification -
washing or partial melting.

impossible. With solid carbon dioxide as the refrigerant, COD material balances were reasonably satisfactory, and purification results for contaminants other than COD seemed about the same as with the isobutane freezing. It is believed that the isobutane caused COD reduction factors to be less than would have been the case if isobutane had been removed.

A rough and preliminary cost estimate for advanced waste treatment was made for a hypothetical plant having a freezing stage, a melting stage, and two washing stages, with the feed entering one of the washing stages. The estimate assumed counter-current transfer of ice and mother liquor in this process. It was assumed that the same changes in concentration of COD and ABS that were achieved in the better experimental tests could be achieved throughout this plant. On this basis it appears that a 95 percent yield of water with 90 percent of the feed impurities removed can be achieved at a cost somewhat lower than that predicted for desalting sea water by a similar process. The cost estimate contains various approximations and judgments made necessary by the incomplete and variable data. While not rigorously defensible, it is believed to indicate the general neighborhood of the costs and, of course, the areas in which more work is needed.

Recommendations are given on the nature and magnitude of a second phase of investigation of freezing as a method of advanced waste treatment.

INTRODUCTION

This final report on Contract SApH 76969 on freezing as a method of advanced waste treatment contains a condensed summary of all the data (Table 1), some observations during the tests, a description of a possible process for achieving water renovation by partial freezing, an estimate of the cost of such renovation, including mention of possible cost reduction, and a comparison with sea-water desalting by freezing methods. Recommendations for further work are also included.

Tests I through VIII were made in the 6-inch diameter, 4-foot high vessels of the 40-gpd Rose Process pilot plant with isobutane as the refrigerant. Runs IX, X, XII, XIII, and XIV were made in a large battery jar with powdered dry ice as the freezing agent. Run XI was conducted in a home-type ice cream freezer in an attempt to exclude foreign matter completely. In all these runs, secondary effluent from the Pennsylvania State University waste treatment plant (trickling filter) was used as the feed water.

Appendix A gives details supporting the cost estimate in terms of the correspondence of experimental test data with the concentration improvements assumed in the proposed process and plant used to make the cost estimate.

CONDENSED SUMMARY OF ALL THE DATA

A condensed summary of all the data is given in Table i. The product purity values are based on analyses of the last half of the melting ice after it was washed. For example, in Test XIV the entire melt (melt samples 1 through 7) was 7.12 liters, and samples 5, 6, and 7 amounted to 3.48 liters or about one-half. These last three analyzed 16, 16, and 11 ppm COD for an average of 14 ppm given as product purity in Table 1.

OBSERVATIONS DURING TESTS

During freezing, there was little tendency for the feed to supercool before the first ice crystals were formed, and there was no need to seed the cooling liquid with ice crystals to avoid supercooling and consequent flash formation of ice. This supercooling and flash formation (very rapid or sudden formation of ice) are sometimes encountered with salt-water feeds and must be avoided by suitable precautions in operation of salt-water processes. Apparently the extra precautions are not required for waste water. Ice crystals appeared larger than those formed in desalting operations in similar apparatus. The entire washing process seemed similar to that used in desalting. Melting also was similar to the melting of ice from saline water. In some tests, small areas of dark films, presumably suspended impurities from the secondary effluent feed, appeared at the melting ice surface, but these did not interfere with the rate of melting, nor could they be associated with variations in results.

POSSIBLE PROCESS

Figure 1 is a schematic flow diagram for a plant or process for advanced waste treatment by partial freezing with a liquid hydrocarbon refrigerant such as isobutane. Auxiliary equipment, such as heat exchangers, compressor, and isobutane strippers, is not shown, because it is similar to that used in desalting plants. The actual numbers used for the concentrations of impurities and the relative flows are based on the arbitrarily selected requirement of removing 90 percent of the impurities (reducing COD from 100 ppm to about 10 ppm) and obtaining 95 percent yield of purified effluent. It was felt that this was a reasonable first goal for discussion purposes, and this goal minimizes the work of

making the cost estimate, since relatively direct comparisons can be made with the experimental data, and the over-all equipment required is similar to that for a desalting plant.

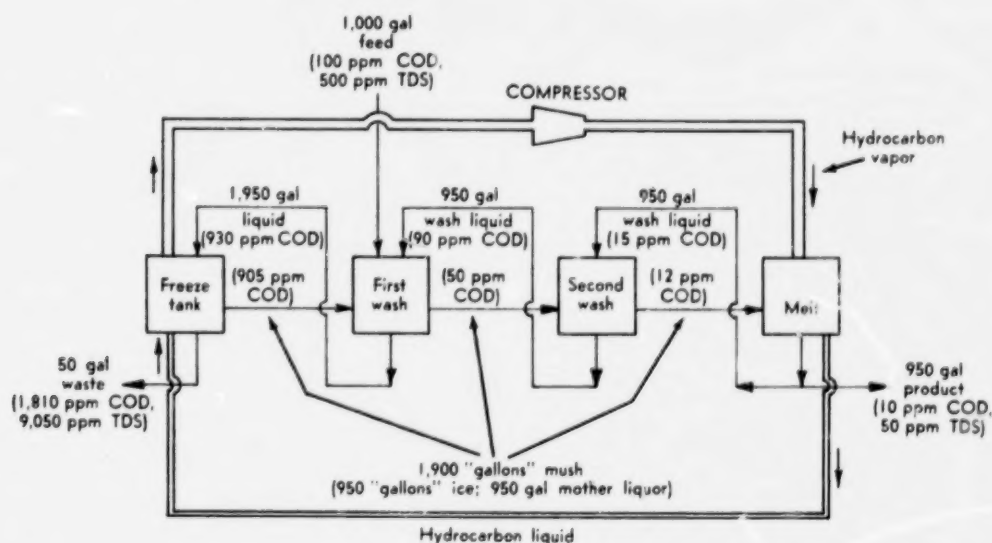


Figure 1. Flow diagram of advanced waste treatment plant.

In the proposed process shown in Figure 1, the freeze tank and the first wash tank concentrate the impurities in the waste, a process that can be compared to the stripping section of a fractional distillation column. The second wash and partial-melt wash are comparable to the rectifying section of a fractional distillation column.

In the process considered here, feed enters the first wash tank along with wash liquid from the second wash tank. As this mixture of liquids contacts the ice mush coming into the first wash tank from the freeze tank, the liquid stream displaces some of the relatively impure mother liquor from the mush so that the mush contains less impurities when it leaves the first wash tank. The liquid leaving this first wash tank has picked up impurities and carries these into the freeze tank. Here the impure liquid is partially frozen, which concentrates the impurities in the mother liquor. Some of this mother liquor is drained off as the concentrated waste stream leaving the process. The ice formed in the freeze tank is in the form of mush because of mother liquor held between the ice crystals. This mush passes to the first wash tank where it encounters the mixture of feed and wash liquid, as already described; the washed ice mush then passes to the second wash tank where it encounters relatively pure wash water from the melt tank. This wash water picks up impurities from the mush, then the wash water passes to the first wash, and the purified mush goes to the melt tank. Here the mush is melted; part becomes the desired renovated product, and part returns to the second wash.

The proposed plant-operating conditions for the second-wash and melt stages were approximately duplicated in the laboratory tests of the present contract. The conditions for the freeze tank and first wash were not used in the tests, but the data indicate that the concentrations used in Figure 1 can probably be achieved. This is believed likely because, in the later test runs of the present contract in which the best separation was achieved, the gross contamination (considering chloride and conductivity data as well as COD) was reduced by a factor of about 10 in many cases. This tenfold reduction was in an experimental operation that corresponded to the second-wash and melt process alone.

In the proposed plant, the first wash uses twice as much wash water as the second wash, so it seems likely that, with this additional wash water, the necessary factor of 18 would be approached in the first wash. It is to be noted that the experimental ratios for chloride and for conductivity are appreciably higher than those for COD. In the proposed plant, however, this ratio is taken, conservatively, to be the same as for COD. A probable cause for the relatively low COD ratios is the isobutane in the product, so that, with isobutane removed, these ratios would be increased.

There is also some evidence that the second-wash and the partial-melt steps could be combined and made to carry the full rectification burden, or at least most of it. Early runs had poor separation during washing, but good separation during melting. In the later runs, where washing was efficient, improvement in the effluent from partial melting was much less pronounced. Possibly the product improvement had leveled off owing to difficulties in analysis, or to contamination, or to the presence of some inseparable material. If so, it might be possible to start with a feed several times more concentrated and still end with product water substantially as good.

Characteristics of Process

There is a variety of specific ways in which a partial freezing process could be arranged and operated. The process discussed here is essentially a repetitive batch process in which ice mush is moved through several discrete washing stages countercurrent to the wash liquid. For purposes of the present explanations and discussion, it is assumed that the ice mush is actually moved by suitable mechanical devices from the freezing stage to first wash, to second wash, to melt. In practice, it is not actually necessary to move the ice, but the means of achieving this are not important for the present purposes. Also in practice, it might be desirable to make the process more or less truly continuous. For the present discussion, it is preferable to assume that a batch of ice is produced in the freeze tank, while washing of two previous batches

is going on in the wash stages, and a still earlier batch is being melted. When these operations are completed, the melt tank is empty, the ice mush in wash tank 2 can be moved to the melt tank, the ice mush in wash tank 1 can be moved to wash tank 2, and the freshly frozen ice can be moved from the freeze tank to wash tank 1.

This type of process was chosen here because it provided a relatively easy way to develop an understandable explanation to support the cost estimate. Other ways of operating, such as a truly continuous countercurrent process, or a semi-continuous operation, or a batch-cyclic operation without moving the ice, can all be expected to give the same general results, but to have operating advantages or disadvantages. U. S. Patent Application 805,834 (April 13, 1959), by Arthur Rose, describes a batch-cyclic freezing process for application to desalting of saline water and for other purifications.

COST ESTIMATE

Since the partial freezing process was shown to remove impurities, and the data gave some indication of the type of plant and operating conditions that might be used, a rough, preliminary cost estimate can be made.

The general approach for arriving at a cost estimate was as follows. It was desired to use the existing cost estimate information for the Rose Freezing Process for desalting sea water, to avoid detailed estimating. A process was arbitrarily chosen, therefore, that had two washing stages plus freezing and melting stages, and relative flows the same, as far as possible, as in the desalting process. Specifically, a mush with 50 percent ice and 50 percent mother liquor was used in the final (second)-wash stage. In the melt stage, half of the melt was returned as wash water. For example, as illustrated in Figure 1, 1,900 gallons of mush entered the melt stage and 950 gallons of wash liquid were returned to the second-wash stage. The other flows, and the concentrations, were adjusted by trial and error and material balance to produce 90 percent reduction of impurities in the feed and a 95 percent yield of purified water. This degree of purification was selected because it was a reasonable goal and because its use gave concentrations and purification ratios in the proposed plant that corresponded fairly well with those obtained in the experimental tests. Details of this correspondence, which are, of course, essential to support the following cost discussion, are given in Appendix A.

A plant to produce a million gallons per day of desalinated water by the Rose Freezing Process had been designed and costed in some detail by the authors prior to beginning the present

waste treatment work. The information from this design work can be used to arrive at a rough but reasonable cost estimate for the waste treatment because the number of stages and, in general, the amount of equipment is similar for both the desalting process and for that of Figure 1.

For the desalination plant, the estimated cost of producing water (including utilities, labor, depreciation, capital costs, engineering, buildings, etc.) is about \$0.50 per 1,000 gallons. About 33 percent is power cost, about 18 percent is operating and miscellaneous overhead costs, and 49 percent is capital amortization costs. The principal saving in a waste treatment process over the desalination process arises from the fact that the dissolved matter is much smaller in concentration, and this results in a lower freezing-point depression and less power consumption. Moreover, a larger part of the processed feed can go to product. As a consequence, the cost of precooling the feed will be lower (a smaller heat exchanger necessary) and the energy for auxiliary heat removal will be less. The energy may be only about 80 percent as much as for desalination. The saving arises from the fact that, in the process under discussion, the freezing point of waste water is not much below 0°C (32°F) while that of sea water is -2.15°C , and the mother liquor from freezing sea water is -4.3°C . Consequently, in a waste-water process, the driving force (pressure differential of main refrigeration compressor) can be reduced to about 60 percent of that in a sea-water process plant. This compression consumes about half the total energy required for the process. The other half is consumed by minor pumps and by the auxiliary compressor that operates over the ambient-process temperature range and takes care of heat gains, pressure drops in lines other than refrigerant lines, and main heat exchanger driving forces. The reduction to 60 percent on the main compressor becomes, therefore, only 80 percent of the over-all energy requirement.

The savings in compression equipment and heat exchangers may cut about 10 percent off the capital and depreciation costs. The operating costs for waste treatment should, therefore, be a few cents less per thousand gallons renovated product water than for the desalting process, and the capital costs for an advanced waste treatment plant using a freezing process can be roughly estimated as about 90 percent of the cost for a sea-water desalting plant using the same process.

Further cost reduction may result from use of less expensive materials for construction, and less corrosive feed, with consequent longer equipment life. The really significant reductions in cost could come through process improvements such as eliminating one wash step or increasing the processing capacity of the equipment by a reduction in reflux ratio, i.e., a reduction in washing requirements. Considerable investigation on a moderate and large scale is needed to bring about these improvements.

Comparison with Desalting by Partial Freezing

In addition to the fact that the concentration of impurities in the secondary waste effluent is on the order of only 2 percent of that in sea water, and that waste water is possibly less corrosive, there are other differences between desalination and waste-water treatment. The aim in desalination is to obtain good water whereas the primary aims of advanced waste treatment are twofold: (1) To concentrate a maximum amount of the impurities in an economically disposable volume of waste water to allow permanent disposal of these contaminants and thereby decrease pollution, and (2) to produce re-usable water. Consequently, recovery must be high for waste-water treating while it need not be necessarily so for desalting. A 50 percent yield of fresh water is satisfactory in desalting, but in complete waste treatment, the renovated stream must be at least 99 percent of the feed stream.

For this last reason, the process presented in Figure 1 is so designed and operated that there is a flywheel effect in the freeze tank. For removal from the process of only 50 gallons of waste, 1,950 gallons of liquor go into the freeze tank, and 1,900 gallons of mush come out and move toward the product end. As a consequence, a long time is required for steady state to be reached after starting such a plant. The product water during the startup period would be pure, but no waste stream is withdrawn until steady state is reached.

In the test runs made, it is evident that the formation of foam in the freezer, caused by the bubbling of the refrigerant through ABS-containing waste water, could be a problem. This could probably be overcome by prefoaming the feed or removing the concentrated foam, in some manner, from the freezer. Adsorption of alkyl benzene sulfonate and other COD-bearing materials on the ice crystals may also occur, and this deserves further study.

RECOMMENDATIONS

In the work of this contract, the purification achieved is sufficient, and the estimated costs are low enough to indicate the desirability of a second phase of investigation on freezing as a method of advanced waste treatment. This further investigation is especially warranted if possible cost reductions are taken into consideration, along with possible advantages of combining freezing with foaming.

It is recommended that a further series of 10 to 20 partial freezing and washing tests with isobutane refrigerant be performed to obtain data for a more reliable cost estimate. The tests should

include some on concentrated waste streams of 9,000 ppm TDS or higher, as would be encountered in the concentrated product of the advanced waste treatment. Some tests should be made on a 1,000-gallon-per-day scale to approach the scale-up problem. The objective throughout should be the establishment of dependable relations between extent of partial freezing, rates of flow in washing, quantities of wash liquid, and purity of product streams. This investigation should certainly incorporate a degassing operation in the process or in the COD analysis to eliminate isobutane from COD values. All aspects of the sampling and COD-analyzing procedure should be standardized, including the time between sampling and analyzing. The test program should also include some investigation of intentional amplification of foaming during partial freezing as a possible means of improving the removal of detergents. Unless the removal of detergents by foaming appears to be a successful and complete solution, a separate series of small-scale, partial freezing experiments should be done to establish the fate of detergents in the freezing operation. The test results should be evaluated by a description of process operability and a cost estimate.

Preliminary comparison should be made between a fixed-ice bed and a moving-ice bed process. Centrifugation as a high-capacity, high-separation process should be examined as an alternative to simple gravity draining. The possibility of performing actual tests in existing saline-water pilot plants should be explored and recommendations made.

APPENDIX A

Comparison of Concentrations in Proposed Plant and in Test Experiments

Throughout this discussion, impurities have been assumed to be COD only, but the same reasoning applies to other kinds of impurities, such as chlorides, conductivity-causing materials, and ABS, if they behave as in Tests VIII, XI, XII, or XIII. The discussion will be divided into two parts. The first part will show that the experiments on washing were done under conditions similar to those selected for the second-wash and melt steps of the proposed waste treatment plant of Figure 1.

The proposed plant has a flow of 1,900 gallons of mush from the first-wash stage to the second-wash stage. This mush consists of 950 gallons of actual ice mixed with 950 gallons of mother liquor. The liquor contains about 100 ppm of COD impurities, so the mush contains about 50 ppm. In the experiments, a comparable situation occurred in the washing operations after partial freezing and draining of the easily drained portion of the mother liquor. The COD impurities in this mother liquor ranged from 68 to 270 ppm. The drained mush was not analyzed, but was wet with this same mother liquor; the percent actual ice in this drained mush averaged about 50. Hence, the mush in the test experiments would have analyzed about 34 to 135 ppm COD.

In the proposed plant, the 1,900 gallons of mush entering the second-wash stage is washed with half this volume of melt. The melt is assumed to contain about 15 ppm of COD impurities. In the experiments, the drained mush was washed with about half its volume of fresh water, which often analyzed in the range 10 to 30 ppm of COD impurities.

In the proposed plant, the washings from the second wash are assumed to contain an average of about 90 ppm of COD impurities. In actuality the average would be higher than this at the start and lower at the end of the wash, possibly as low as 25 ppm. In Test XIV, the washings ranged from 111 to 38 ppm COD.

In the proposed plant, the 1,900 gallons of mush from the second wash goes to the melt stage. The 950 gallons of liquor in this mush is stated to contain about 25 ppm impurities, making about 12 ppm in the total mush. No measurements were made on the corresponding mush in the test experiments.

In the proposed plant, the 1,900 gallons of mush from the second wash is melted in the melt stage. The first 950 gallons of melt is used as "reflux" for washing in the second-wash stage. As already mentioned, this reflux is assumed to average about 15 ppm impurities, the first portion having 25 and the last possibly as low as 10. In Test XIV, the COD in the melted ice ranged from about 29 at the start, to 20 at the middle, and 11 at the end of the melt.

Thus, there is at least a rough correspondence between the concentrations and flows in the experiments and those in the second-wash and melt stages in the proposed plant. The experimental support for the concentrations in the first-wash and freezing stages of the proposed plant is less certain but still believed reasonable.

In the proposed plant, there is 1,900 gallons of mush coming from the freeze tank to the first-wash stage. This mush is made up of 950 gallons of actual ice and 950 gallons of mother liquor. The mother liquor contains about 1,800 ppm of COD impurities. In the first wash of the proposed plant, the 1,900 gallons of mush is first washed with 1,000 gallons of feed containing 100 ppm COD impurities. The first washings are presumed to be of the 1,800 ppm mother liquor concentration, but the later washings must be much lower, because the 100 ppm feed liquor is displacing the 1,800 ppm mother liquor.

After the 1,000 gallons of feed is used as wash, the 950 gallons of liquor coming from the second-wash stage is used to further wash the 950 gallons of actual ice in the first-wash stage. As already mentioned, the wash from the second-wash stage may be expected to be as low as 25 ppm COD in the very last of the 950 gallons. The end result of the first-wash operation is to transfer back to the freezing stage 1,000 gallons of washing displaced by the feed wash, and then 950 gallons displaced by the wash from the second wash. The first portion of these washings is assumed to contain 1,800 ppm COD, the last considerably less (possibly as low as 150 ppm), and to average 930 ppm. The liquor finally left with the ice when the first-wash operation is completed is assumed to average about 100 ppm COD; this is the mush that goes to the second-wash stage already described.

Thus, the first-wash operation converts a mush of 950 gallons actual ice and 950 gallons mother liquor with 1,800 ppm impurities to a mush of 950 gallons actual ice and 950 gallons liquor with only 100 ppm impurities in the liquor. Since no test experiments were done in the concentration range 200 to 2,000 ppm COD, the experimental support for the concentration changes in the freezing and first-wash stages is based on the assumption that the ratio of concentrations would be the same above 200 ppm as the experiments showed it was below 200 ppm.

Below 200 ppm, the best experiments (Tests XIII and XIV) show about a 3-to-1 ratio between impurities in mother liquor before washing and mother liquor after washing, when a quantity of wash is used equal to the amount of mother liquor held in the mush. Hence, in Test XIV, the mother liquor had 111 ppm COD, while the concentration of the last portion of the wash (midpoint between Drain 4 and Melt 1) was the average of 46 and 29, or 37 ppm COD. The isobutane probably caused the above-mentioned ratio to be lower than it would have been without isobutane. In the latter case, the ratio would be expected to be nearer the ratios for chlorides and conductivity, i.e., 5 to 1.

If this ratio of improvement holds for COD above 200 ppm, then the 1,800 ppm mother liquor would be reduced four-fifths of the way to 100 ppm (i.e., to about 450 ppm) by the 1,000 gallons of feed wash; the 950 gallons of mother liquor from the second wash (with final impurities of 25 ppm) would further reduce the impurities four-fifths of the way from 450 to 25 ppm or to about 120 ppm, which is somewhere near the desired 100 ppm of the liquor in the mush going to second wash.